

REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-04-

0018

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1. REPORT DATE (DD-MM-YYYY) 01-11-2003		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 1998 - 2000	
4. TITLE AND SUBTITLE Tailoring the Poisson Ratio: Design Concepts for New Polymeric Materials				5a. CONTRACT NUMBER F49620-98-1-0078	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Anselm C. Griffin				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) The University of Southern Mississippi Hattiesburg, MS 39406				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Office of Scientific Research 801 N. Randolph St., Arlington, VA 22203-1977				10. SPONSOR/MONITOR'S ACRONYM(S) AFOSR/PKC	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approve for Public Release: Distribution Unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT This report describes work toward the establishment of design criteria for producing polymeric materials having a negative Poisson ratio. This unusual mechanical behavior is also known as auxetic behavior and is characterized by a material getting fatter when stretched. Our approach deals with a molecular-scale concept by which a nematic liquid crystalline field orients rigid rods in a main chain polymer - some of which are attached to the chain at lateral positions along the rod as opposed to attachment at the ends of the rods (terminal attachment). The nematic field-induced parallel orientation of all rods is subsequently overcome by a mechanical field when stretched. The side-attached rods will then orient roughly normal to the stretch direction resulting in an increase in the interchain separation and to an auxetic response. We have made model compounds to examine this concept; a series of nematic polymers having end- and side-attached rods; and crosslinked nematic polymers having end- and side-attached rods. X-ray data is consistent with our postulated effect and mechanical testing has shown a strong sensitivity to the molecular structure.					
15. SUBJECT TERMS auxetic; negative Poisson ratio; nematic polymer; molecular-level auxetics					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES 8	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (Include area code)

Final Report

AFOSR Award F49620-98-1-0078

Anselm C. Griffin

Introduction

This project was built around the desire to establish design rules for creating molecular-level auxetic polymers. These materials get fatter when stretched (negative Poisson ratio) which should allow them to be of utility as reinforcing fibers in composites, as seals and gaskets, as fasteners, as fibers and plastics in personnel protecting clothing for projectiles, and many other applications for which this extremely rare deformation behavior can be used to advantage. Our interests are in establishing molecular design rules and concepts to permit tailoring the auxetic effect (negative Poisson ratio) in polymeric materials in which the physical mechanism for creating the auxetic effect is directly related to the detailed chemical structure at the molecular level. Our approach is to create polymers in which both laterally-attached rigid rods and terminally-attached rigid rods are used – with flexible spacers to connect the rods - to create the polymeric main chain. The laterally-attached rods will orient parallel to the other terminally-attached rods in a main chain liquid crystalline polymer due to the rod-ordering effect of a nematic (liquid crystalline) field. Upon stretching of the sample, the site-attachment of the laterally-connected rods will drive them to a position approximately perpendicular to the stretching direction, thus increasing the

lateral interchain distance in the polymer which will, in turn, increase the width of the sample producing an auxetic response – increase in width accompanying an increase in length. In simple terms, the mechanical field is used to overcome the rod-ordering effect of the nematic field. This behavior should be reversible.

Model Compound Studies

Critical to our approach is that the (modified) polymer having both laterally-attached and terminally-attached rods must be liquid crystalline. The laterally-attached rods (sometimes called 'transverse rods') cannot cause the polymer to lose its liquid crystalline behavior. To confirm that premise with model compounds, a total of six model compounds containing terphenyl transverse rods were synthesized and studied. All of these compounds displayed liquid crystalline phase behavior. Model compounds containing longer transverse rods caused only a small destabilization of the mesophase when compared with their shorter transverse rod counterparts. This result suggests that the transverse rods in these model compounds are roughly oriented along the nematic director. This is a critical component in the site-connectivity concept for driving auxetic response.

Our results also showed that a ten carbon alkylene chain spacer is long enough to allow the terphenyl transverse rods to orient in the nematic field. Furthermore, it was found that increasing the length of the terminal rods by

adding additional para-substituted phenyl groups (5-phenyl ring rods) leads to a significant increase in the stability of the mesophase. This is due to the increased anisotropy of the longer terminal rods.

Linear Polymers

For study of the linear polymers themselves, nine linear polymers containing transverse rods were synthesized and examined. These nine polymers differed among themselves in that they contained different lengths of transverse rods (terphenyl with hydrogen, terphenyl with propyl, and pentaphenyl with propyl); different percent compositions of the transverse rods relative to the total rods present (16.7%, 25%, and 33.3%); and different lengths of the flexible spacers (4 and 10 carbon alkylene chain). All of these polymers were nematic liquid crystalline polymers, as was the parent polymer – a nematic polyester containing phenyl benzoate rod units.

Examination of these polymers revealed that with increasing percentages of the transverse rod component, the thermal stability of the nematic phase in these polymers decreased. This is not unexpected due to the 'bump' or 'curve' structure in these polymers caused by the flexible spacer having to accommodate itself within the ordered liquid crystalline arrangement and is not simply due to the presence of the transverse rods themselves. It was also seen that the longer transverse rods (5-ring) do not destabilize the mesophase when compared with their shorter transverse rod counterparts

(3-ring). This result is at first surprising, but can be rationalized when one considers that - with the longer transverse rods - it is these 5-ring rods which define the nematic phase stability. These longer rods are dominating the more abundant shorter rods in determining the mesophase stability. This suggests that the transverse rods are roughly oriented along the nematic director.

The interplay of rigid rod length / flexible spacer length, and the energetics of the various nematic packing structures is complex. There are likely two extreme types of packing patterns that co-exist in these linear polymers. One we call the co-linear packing pattern (all rods in a segment of the main chain are co-linear) and the other, the zigzag packing pattern (in a given segment of the main chain, rods are parallel, but not co-linear) . We feel that longer transverse rods and shorter spacers favor the zigzag packing pattern. This is due to the large physical and energetic barriers incurred by attempting to arrange the longer transverse rods, or transverse rods with shorter spacers, along the same line (co-linear) as the polymer main chain. By contrast, shorter transverse rods and longer spacers could favor the co-linear packing pattern.

Polymers with highly regular repeating units in which the alternation between transverse and terminal rods along the main chain is regular, not random, have sharp phase transitions. By contrast, the other, random, copolymers

have broad phase transitions. This is most likely due to advantageous packing arrangements for polymer chains with highly regular chemical structures in their ability to form a uniform, homogeneous nematic phase. It was found that reducing the length of the flexible spacer attached to the transverse rods from ten carbons to four carbons, surprisingly, does not destabilize the mesophase. For the four carbon spacer the most likely arrangement is for the zigzag packing pattern to dominate. For this zigzag packing pattern, a shorter spacer can allow the transverse rods to orient with the liquid crystalline director in a parallel, but not co-linear fashion. In this zigzag alignment for the shorter spacer, the oriented transverse rods will not disrupt the nematic packing order of the polymer chains.

Crosslinked Polymers

Using the same parent nematic polymer along with our transverse rod chemistry, we also examined crosslinked polymers with different degrees of crosslink density. Introduction of a large, flexible cyclotetrasiloxane crosslinking agent reduced the crystallinity of the parent polymer. A crosslinked polymer with 4.5% crosslink density was found to be totally amorphous as indicated by the disappearance of the crystallization peak in the DSC scan. These crosslinked polymers retained their liquid crystallinity. As anticipated, their clearing temperatures decreased somewhat as the crosslinking density increases. Crosslinking of the liquid crystalline polymers reduces mobility of the polymer chain segments. Therefore, at high crosslink

density, orientation of these nematic chain segments is more difficult. This leads to a decrease of the clearing temperature with increased crosslinking.

For the auxetic effect we wanted polymers with low glass transitions to observe the effect at ambient temperatures. Unfortunately, the glass transition temperatures of our crosslinked polymers are not reduced by the introduction of the cyclotetrasiloxane crosslinking agent. The parent nematic 10,10 polyester structure still dominates the thermal behavior resulting in no change to the glass transition temperature with crosslinking.

As an example of our results with crosslinked polymers, the polymer network with 4.5% crosslinking density and 16.7% pentaphenyl transverse rod component retains its liquid crystallinity but the nematic-isotropic clearing temperature is significantly lower than that of its counterpart without the transverse rod. As might be expected, this polymer is also completely amorphous.

X-Ray Analysis: Interchain Separation

An increase in the interchain packing distance when stretched is an indirect evidence of auxetic behavior in our polymers. The most powerful way to probe the average polymer interchain distance is by use of X-ray scattering. For our polymers X-ray analysis was carried out on a Siemens X-ray diffractometer. The general idea was that by measuring the average

interchain distances of two types of polymer samples - unstretched and stretched - using X-ray analysis, we can know the average interchain distances of the polymers before they were stretched and after they were stretched.

In X-ray scattering, the equatorial scattering provides information regarding interchain packing distances. Our X-ray results revealed that, for polymers having a transverse rod, stretching the sample produced an increase in the interchain separation when compared to the parent polymer with no transverse rods. Also, when comparing transverse rods of differing lengths, the longer transverse rods produced a greater interchain separation upon stretching as predicted from our model. All our x-ray results were consistent with our conceptual model which confirms our approach - incorporating transverse rods into nematic polymers to effect an auxetic response - as valid. We have participated in a collaboration with the group of Professor Ken Evans at Exeter for experimental investigation of the mechanical behavior of our polymers. The Exeter group has obtained interesting results for some of our polymers indicating a highly anisotropic Poisson ratio in which the Poisson ratio is considerably different in the xy direction as compared with that in the xz direction.

Personnel:

In addition to Dr. Anselm C. Griffin as PI on the contract, Puwei Liu, a PhD student at the University of Southern Mississippi was mainly involved with the experimental portion of this work. He graduated in August, 2000, with a PhD based on his dissertation "Design, Synthesis, and Characterization of Liquid Crystalline Polymers and Networks Containing Transverse Rods for Potential Auxetic Materials". We also had assistance from both Dr. Chaobin He, a postdoctoral associate, and Dr. Chad Booth, then a PhD student, in x-ray and mechanical studies of the polymers made by Puwei Liu.